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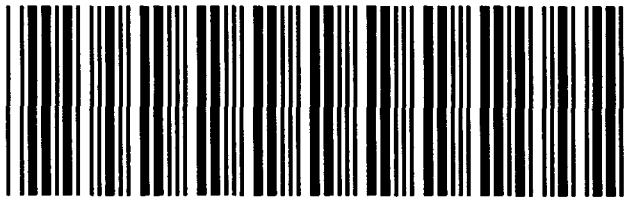

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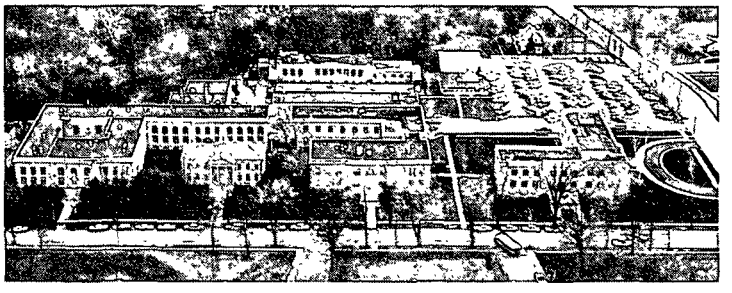

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DEGRADATION OF A NONREDUCING CELLULOSE MODEL, 1,5-ANHYDRO-4-O-β-D-GLUCOPYRANOSYL-D-GLUCITOL, UNDER KRAFT PULPING CONDITIONS

DAVID A. BLYTHE AND LELAND R. SCHROEDER

NOVEMBER, 1984

DEGRADATION OF A NONREDUCING CELLULOSE MODEL, 1,5-ANHYDRO-4-O-β-D-GLUCOPYRANOSYL-D-GLUCITOL, UNDER KRAFT PULPING CONDITIONS[1,2]

David A. Blythe[3] and Leland R. Schroeder[4]
The Institute of Paper Chemistry
Appleton, Wisconsin 54912

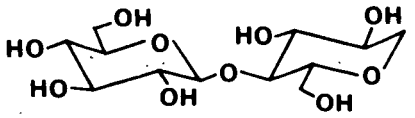
ABSTRACT

The title compound (1, 1,5-anhydrocellobiitol) was degraded at 170°C in kraft pulping liquor (1.0M NaOH, 0.2M Na_2S) to determine whether the sulfur anions affect the rate-determining and/or product-determining steps of glycosidic bond cleavage. Since the extent of hydrolysis of S^{-2} to form HS^- and HO^- was unknown, 1 was also degraded in NaOH solutions simulating total hydrolysis (1.2M NaOH, 1.4 μ) and no hydrolysis (1.0M NaOH, 1.4 μ). The proportion of glycosyl-oxygen bond cleavage (88%) and oxygen-aglycon bond cleavage (12%) was the same in all three cases. The rate constant for degradation of 1 under the kraft conditions was equal to that for the NaOH control degradation simulating total hydrolysis of S^{-2}, but greater than that for the control simulating no hydrolysis. This indicates that S^{-2} is hydrolyzed under these kraft conditions to HS^- and HO^-, and that HS^- does not participate in the rate-determining steps of glycosidic bond cleavage. Since HS^- is a stronger nucleophile than HO^-, these results also imply that HO^- does not cleave the glycosidic linkage by S_N2 mechanisms. The yields of 1,6-anhydro-β-D-glucopyranose (4) from glycosyl-oxygen bond cleavage and 1,5-anhydro-D-glucitol (2) from oxygen-aglycon bond cleavage were lower for degradations of 1 in the kraft liquor than in the NaOH controls. This is due to HS^- involvement in the product-determining steps of the degradation of 1.

INTRODUCTION

The viscosity of the pulp decreases substantially during alkaline pulping of wood due to random cleavage of the cellulosic chains.[5-8] The sulfide present in kraft pulping liquor is generally believed not to participate in the cleavage reaction.[5-7] In contrast, the sulfide probably effects decreased carbohydrate degradation by accelerating the rate of lignin removal, thereby reducing the time which the carbohydrates are exposed to the alkaline pulping liquor.[6,7,9] The base-catalyzed, intramolecular $S_Ni cB(2)$ mechanism[10] generally assumed to be operative in cellulosic cleavage[5-8,12-14] would account for nonparticipation of the kraft liquor sulfur nucleophiles (sulfide dianion and hydrosulfide anion) in the reaction. However, an intermolecular S_N2 mechanism for cellulosic chain cleavage has been speculated upon,[13,15] and some simple alkyl[16] and aryl glycosides[15,17,18] have been reported to degrade by bimolecular mechanisms. For the S_N2 mechanism, the sulfide and hydrosulfide ions, which are believed to be stronger nucleophiles than hydroxide ion,[19] could increase the rate of glycosidic bond cleavage. In addition, S_N1 mechanisms appear to be viable for cellulosic chain cleavage.[11] For the unimolecular mechanisms, the kraft liquor sulfur nucleophiles would not affect the rate of chain cleavage, but could be involved in product-determining steps of the overall reaction.

In this paper we report the results of a study of the degradation of a nonreducing cellulose model, 1,5-anhydro-4-O-β-D-glucopyranosyl-D-glucitol (1) (1,5-anhydrocellobiitol) under kraft pulping conditions. Our objective was to determine whether the sulfur nucleophiles in the kraft liquor affected the rate-determining or product-determining steps of glycosidic bond cleavage in 1. Previously, we reported the results of an extensive study of the degradation of 1 in aqueous, oxygen-free sodium hydroxide.[11]



1

RESULTS AND DISCUSSION

Kraft reaction solutions contained 1.0M sodium hydroxide and 0.2M sodium sulfide, similar to industrial pulping liquors.[15] The sodium sulfide hydrolyzes according to Equations 1 and 2.

$$S^{-2} + H_2O \rightleftharpoons HS^- + HO^- \quad (1)$$

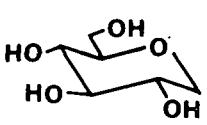
$$HS^- + H_2O \rightleftharpoons H_2S + HO^- \quad (2)$$

The first dissociation constant of hydrogen sulfide (pK_a1) is about 7.0 at 25°C and reportedly varies by only 0.5 up to 200°C.[20] Therefore, the equilibrium in Equation 2 lies fully to the left and virtually no hydrogen sulfide is present in kraft pulping liquors. The second dissociation constant of hydrogen sulfide (pK_a2) is not known with as much certainty. At 170°C, values between 11.0 and 12.5 have been proposed for pK_a2.[20] Thus, it is not as evident where the equilibrium in Equation 1 might lie in kraft pulping. It is possible that the relative importance of the sulfide dianion and the hydrosulfide anion could change as the pH and temperature of the pulping liquor change. However, data from kraft pulping of wood and cotton linters indicate that the sulfide ion is essentially hydrolyzed to hydrosulfide ion, with concomitant formation of hydroxide ion (Equation 1), under these conditions.[21-23]

Since the rate of degradation of 1,5-anhydrocellobiitol (1) depends on the hydroxide ion concentration,[11] and since the degree of hydrolysis of the sulfide dianion which forms more hydroxide ion was uncertain, two control reactions in aqueous sodium hydroxide were required. One reaction was performed in 1.2M sodium hydroxide with an ionic strength of 1.4 μ. This reaction

corresponds to the sodium hydroxide concentration and ionic strength of the kraft liquor if the sulfide dianion is completely hydrolyzed. The second control reaction was performed in 1.0M sodium hydroxide with an ionic strength of 1.6 μ. This reaction models the kraft liquor if the sulfide dianion is unhydrolyzed.

The stable products identified from the degradation of **1** were 1,5-anhydro-D-glucitol (**2**) and 1,5:3,6-dianhydro-D-galactitol (**3**). In addition, 1,6-anhydro-β-D-glucopyranose (**4**) was identified as a reactive intermediate.



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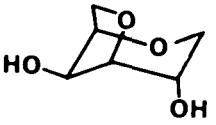

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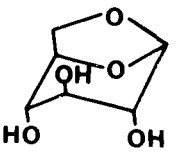

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Since the sodium hydroxide concentration in all of the reactions was large relative to the concentration of **1**, the disappearance of **1** and the appearance of stable products **2** and **3** followed pseudo-parallel-first-order kinetics (Equations 3, 4, and 5; Figure 1).[24,25]

$$\ln (X_{r,t}) = - k_r t \quad (3)$$

$$\ln (X_{i,\infty} - X_{i,t}) = - k_r t + \ln (X_{i,\infty}) \quad (4)$$

$$k_i = k_r X_{i,\infty} \quad (5)$$

where $X_{r,t}$ is the mole fraction of reactant at time t, $X_{i,t}$ is the mole fraction of product **i** at time t, $X_{i,\infty}$ is $X_{i,t}$ at completion (the relative proportion of product **i** formed), k_r is the pseudo-first-order rate constant for reactant disappearance, and k_i is the pseudo-first-order rate constant for formation of product **i** ($\Sigma k_i = k_r$).

Fig. 1 here

Rate constants for the degradation of **1** and the mole fractions

TABLE 1

Rate constants and product mole fractions for degradations of 1,5-anhydrocellobiitol (1) at 170.0°C

NaOH, M	Na_2S, M	NaOTs,[a] M	μ	$10^6 k_r$,[b] s^{-1}	Product Mole Fractions ($X_{i,\infty}$)[c] 2	3	4	$Y_{4,\infty}$[d]
1.0	0.2	--		6.80±0.08	0.875	0.084	0.328	0.375
1.2	--	0.2	1.4	6.77±0.07	0.881	0.103	0.368	0.418
1.0	--	0.6	1.6	6.16±0.06	0.876	0.104	0.386	0.441

[a] Sodium p-toluenesulfonate.

[b] Pseudo-first-order rate constant for degradation of 1, adjusted to 170.0°C, average of three determinations.

[c] 1,5-Anhydro-D-glucitol (2), 1,5:3,6-dianhydro-D-galactitol (3), and 1,6-anhydro-β-D-glucopyranose (4).

[d] Mole fraction of 4 formed, based only on glycosyl-oxygen bond cleavage ($X_{4,\infty}/X_{2,\infty}$).

for products 2 and 3 are reported in Table 1. Rate constants for product formation can be calculated from the data in Table 1 using Equation 5.

Rate constants (k_f) for formation of 1,6-anhydro-β-D-glucopyranose (4) from 1 were calculated from the linear relationship [Equation 6, Figure 2] describing the concentration of 4 as a function of time.[11,25]

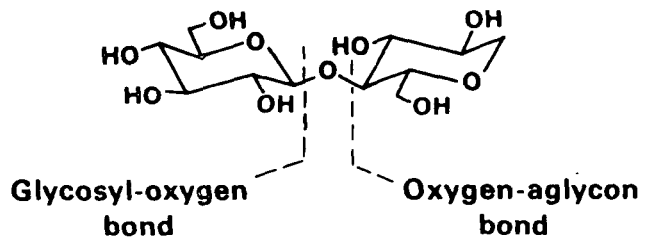
$$L-L_oe^{-k_dt} = k_fR_o\ (e^{-k_rt} - e^{-k_dt})/(k_d-k_r) \qquad (6)$$

where L is the concentration of 4 at time t, L_o is the initial concentration of 4[26], R_o is the initial concentration of 1, k_r is the rate constant for degradation of 1, and k_d is the first-order rate constant for degradation of 4. Values for k_d were determined independently for each set of reaction conditions.[27]

Fig. 2 here

The mole fractions of 4 formed in degradations of 1 ($X_{4,\infty}$, Table 1) were calculated as the ratio k_f/k_r. Since 4 degrades at these reaction conditions, $X_{4,\infty}$ is actually zero. Conceptually, however, $X_{4,\infty}$, as calculated, is the mole fraction of 1 which degrades via 4 without reference to the subsequent fate of 4.

Previously, it was shown that 1 degraded in aqueous sodium hydroxide by both glycosyl-oxygen and oxygen-aglycon bond cleavage. 1,5-Anhydro-D-glucitol (2) was formed exclusively by glycosyl-oxygen bond cleavage while oxygen-aglycon bond cleavage resulted in the formation of 1,5:3,6-dianhydro-D-galactitol (3) and fragmentation products.[11]



The rate constant (k_r) for degradation of **1** in the kraft liquor at 170°C was essentially equal to that for the sodium hydroxide control (1.2M NaOH; 1.4 μ) representing total hydrolysis of the sulfide ion to hydrosulfide ion (Table 1), but significantly greater than that for the sodium hydroxide control (1.0M NaOH; 1.6 μ) representing no hydrolysis of sulfide dianion. In addition, the mole fraction of 1,5-anhydro-D-glucitol (**2**) formed ($X_{2,\infty}$, Table 1) was essentially the same (ca. 0.88) in the kraft and soda reactions. Thus, since **2** results exclusively from glycosyl-oxygen bond cleavage,[11] the rate of glycosyl-oxygen bond cleavage (and of oxygen-aglycon bond cleavage) is the same in the kraft and 1.2M NaOH reactions. This indicates that the same reaction mechanisms are operating at the same relative rates in these two media. This also indicates that the sodium sulfide is hydrolyzed under kraft pulping conditions to hydrosulfide anion with concomitant formation of an equimolar amount of hydroxide ion (Equation 1), but that the hydrosulfide anion does not participate in the rate determining steps of the degradation of **1**. This reinforces the conclusions regarding sulfide hydrolysis drawn from studies of kraft pulping of wood and cotton linters.[21-23]

It should be noted that the data in Table 1 do not specifically exclude the possibility that the sulfide ion is not hydrolyzed. However, if this were the case, the sulfide dianion would have to react with **1** at the same rate as the hydroxide ion, and with the same reaction site specificity. This explanation of the data seems far less plausible than total hydrolysis of the sulfide ion to hydrosulfide ion, and an inability of the hydrosulfide ion to accelerate chain cleavage.

Failure of the hydrosulfide anion to accelerate glycosidic bond cleavage in **1** through an S_N2 mechanism is not due to an inherent lack of nucleophilicity. Hydrosulfide anion is 11 times as effective as hydroxide anion in cleaving the oxygen-aglycon bond of methyl α-D-glucopyranoside by an S_N2 mechanism.[16,27,28] An alternate explanation for no rate acceleration with hydro-

sulfide ion is that the carbon atoms in the glycosidic linkage of 1 (C-1' and C-4) have a low susceptibility to bimolecular nucleophilic attack due to electronic and possibly steric factors. Cleavage of the bond between the glycosidic oxygen atom and C-4 of 1 in aqueous sodium hydroxide occurs unimolecularly (S_N1 mechanism) without nucleophilic assistance.[11] Similarly, hydrosulfide ion is only 1.6 times as effective as hydroxide ion in cleaving the glycosyl-oxygen bond of methyl α-D-glucopyranoside (similar to the bond between the glycosidic oxygen and C-1' of 1), even though this reaction in sodium hydroxide appears to occur by an S_N2 mechanism.[16,27,28]

While the hydrosulfide ion does not participate in the rate-determining steps of the degradation of 1, there is evidence that it participates in the product-determining steps. Cleavage of the glycosyl-oxygen bond of 1 is, in part, the result of an $S_NicB(2')$ mechanism (Figure 3).[11] A rapid equilibrium between OH-2' and its conjugate base (5), in conjunction with a conformational change of the glucopyranosyl moiety to the $^1C_4$ conformation, permits a nucleophilic attack by the C-2' oxyanion at C-1' which displaces the conjugate base of 1,5-anhydro-D-glucitol (6) with concomitant formation of 1,2-anhydro-α-D-glucopyranose (7). The 1,2-anhydride 7 can subsequently yield 1,6-anhydro-β-D-glucopyranose (4) by intramolecular nucleophilic attack at C-1 by the C-6 oxyanion or react in several ways to yield acidic degradation products via a reducing sugar. One of the latter possibilities is nucleophilic opening of the epoxide of 7 by hydroxide ion or hydrosulfide ion to generate the reducing sugar. The fact that the mole fraction of 1,6-anhydride 4 formed from glycosyl-oxygen bond cleavage of 1 ($Y_{4,\infty}$, Table 1) decreased in the kraft reaction (1.0M NaOH, 0.2M Na_2S) relative to the soda control reaction at the same ionic strength (1.2M NaOH, 0.2M NaOTs) indicates that hydrosulfide ion is effectively diverting the 1,2-anhydride 7 from formation of the 1,6-anhydride 4 to acidic product formation.

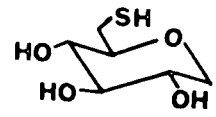
Fig. 3 here

The hydrosulfide ion also affects the products derived from oxygen-aglycon bond cleavage of 1. Degradation of 1 by oxygen-aglycon bond cleavage occurs approximately 12% of the time. The cleavage is believed to occur by an S_N1 mechanism in which heterolysis of the bond forms the β-D-glucopyranosyloxy anion (8) and the 1,5-anhydro-4-deoxy-D-xylo-hexitol-4-cation (9) in the rate-determining step (Figure 4).[11] The glucosyloxy anion 8 would rapidly degrade to acid products.[29] While several product-determining reactions of the cation 9 probably occur, the one leading to 1,5:3,6-dianhydro-D-galactitol (3) dominates. Thus, 98% of the aglycon is accounted for in the sodium hydroxide control reactions (Table 1, Products 2 + 3).

Fig. 4 here

In the kraft reaction the yield of 3 was lower than in the sodium hydroxide control reactions (Table 1). This is probably due to attack by hydrosulfide ion on the epoxides of intermediates 10 and 11 leading from the C-4 cation 9 to 1,5:3,6-dianhydro-D-galactitol (3). Attack by hydrosulfide ion directly on the cation 9 would also be possible, but analogous attack by hydroxide ion does not seem to occur.[11] However, if such a reaction did occur, it would generate the epimers 1,5-anhydro-4-deoxy-4-thio-D-glucitol and -D-galactitol at the expense of 3, with the galactitol isomer predominating due to shielding of the C-4 cation by the departing anion 8.

No evidence of anhydrothioalditols was found in kraft reactions of 1,5-anhydrocellobiitol (1). It was not clear whether these sugars were failing to survive the reaction conditions, or if they were being lost in the analytical procedure. 1,5-Anhydro-6-deoxy-6-thio-D-glucitol (12) was synthesized to test these two possibilities. Compound 12 was shown to be stable in kraft liquor at 170°C over ca. 4 half-lives of 1. However, 12 was retained on the mixed-bed (H^+, OH^-) ion exchange resin used to deionize reaction samples in the usual analytical procedure.



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In an attempt to resolve the analytical problem, reaction samples were deionized with only acidic (H^+) resin prior to acetylation for gas chromatographic analysis. This resulted in the appearance of unidentified products (probably organic acids and lactones) in the chromatograms. These products masked the region of the chromatogram where the anhydrothioalditols were expected to appear, thereby complicating both flame-ionization and specific ion mass spectrometric detection. Elemental sulfur, resulting from the action of the acidic resin on the sodium sulfide, interfered with flame-photometric detection. Thus, direct verification of the anhydrothioalditol products was not obtained.

EXPERIMENTAL

General Methods

Melting points were determined on a calibrated Thomas-Hoover capillary apparatus. Optical rotations were determined on a Perkin-Elmer 141 MC polarimeter. Nuclear magnetic resonance spectra were determined on a Jeol FX100 fourier transform spectrometer at normal probe temperature using tetramethylsilane as an external reference. Elemental analyses were performed by Micro-Tech Laboratories, Inc. (4117 Oakton St., Skokie, IL 60076).

Thin layer chromatography (tlc) was performed on microscope slides coated with silica gel G using methanol-sulfuric acid (4:1, vol) reagent, followed by charring, for component detection.

Gas-liquid chromatography (glc) was performed on a Perkin-Elmer Sigma 2 chromatograph equipped with flame-ionization and flame-photometric detectors, and interfaced with a Sigma 10 data

station. Analyses were performed on a column (5 ft. x 0.125 inch o.d. stainless steel) of 3% OV-101 on 80-100 mesh Supelcoport rigged for on-column injection and using N_2, 30 mL min^{-1}; column, 130°C for 1 min and then 130 → 275°C at 7° min^{-1}; injector, 275°C; and detector, 300°C.

Gas chromatographic mass spectra (glc-ms) were obtained on a Hewlett-Packard 5985 instrument. Electron impact mass spectrometry utilized helium as the carrier gas, a source temperature of 200°C, and an ionizing voltage of 70 ev. Chemical ionization and negative chemical ionization mass spectrometry utilized methane as the carrier gas, a source temperature of 200°C, and an ionizing voltage of 230 ev.

1,5-Anhydro-4-O-(β-D-glucopyranosyl)-D-glucitol (**1**)

Phenyl hepta-O-acetyl-1-thio-β-cellobioside[39] (63 g) in tetrahydrofuran (250 mL) was stirred with W-5 Raney nickel[31] at 48°C for 3 h, and then under reflux for 3 h. The reaction was monitored by tlc using chloroform-ethyl acetate (2:1, vol). If the reduction was not complete, the mixture was cooled to room temperature, more Raney nickel (25 g) was added, and stirring under reflux was continued. On completion of the reaction, the slurry was filtered, and the nickel was carefully rinsed with tetrahydrofuran (3 x 50 mL). The combined filtrates were concentrated *in vacuo* to a crude solid (42 g, 78%) shown by glc to contain at least two by-products. Several recrystallizations from absolute ethanol yielded hepta-O-acetyl-1,5-anhydrocellobiitol (**13**); m.p. 194-195°C, $[\alpha]_D$ + 3.9° (*c* 1.5, $CHCl_3$). [Lit.[11] m.p. 193.5-194.0°C; $[\alpha]_D^{24.5}$ + 4.1 (*c* 2.9, $CHCl_3$)].

Compound **13** was deacetylated with methanolic sodium methoxide[32] to produce **1** which on crystallization from 95% ethanol had m.p. 206-207°C, $[\alpha]_D$ + 28.5° (*c* 1.5, H_2O). ^{13}C-Nmr for **1** (D_2O): δ 103.5 (C-1'), 80.1 (C-4, C-5), 77.0 (C-3', C-5') 76.6 (C-3), 74.3 (C-2'), 70.6 (C-4'), 70.3 (C-2), 69.7 (C-1), 61.7 (C-6'), and 61.4 ppm (C-6). [Lit.[11] m.p. 204.5-205.5°C, $[\alpha]_D$ + 28.2° (*c* 2.2, H_2O)].

showed no absorbance in the 2500-2600 cm^{-1} region characteristic of thiols.[37] ^{13}C-Nmr for **15** (D_2O): δ 86.4 (C-1), 80.9 (C-3), 78.2 (C-5), 73.3 (C-2), 70.6 (C-4), 62.2 (C-6 or C-2'), 62.0 (C-6 or C-2'), and 33.4 ppm (C-1').

1,5-Anhydro-6-deoxy-6-thio-D-glucitol (**12**)

1,5-Anhydro-6-deoxy-6-thio-D-glucitol (**12**) was prepared by the synthetic scheme shown in Figure 5.

Fig. 5 here

Methanesulfonyl chloride (2.4 mL, 1.0 eq.) was added dropwise to a cold (0°C), stirred solution of 1,5-anhydro-D-glucitol (**2**) (5 g) in anhydrous pyridine[38] (100 mL). The mixture was allowed to warm to room temperature and stirred for 3 h. Benzoyl chloride (16 mL) was added dropwise to the stirred mixture, and stirring was continued for 12 h. The reaction was monitored by tlc using chloroform-ethyl acetate (4:1, vol). The mixture was diluted with chloroform (50 mL) and poured into ice water (300 mL). The organic phase was separated and the aqueous phase was extracted with chloroform (2 x 50 mL). The combined chloroform phases were washed with 1M hydrochloric acid (6 x 150 mL), saturated sodium bicarbonate (150 mL), and water (150 mL); and concentrated *in vacuo* to a thick oil. Two crystallizations from absolute ethanol yielded 1,5-anhydro-2,3,4-tri-O-benzoyl-6-O-methanesulfonyl-D-glucitol (**17**) (10.8 g, 64%); m.p. 127-127.5°C, $[\alpha]_D$ +12.6° (c 1.5, $CHCl_3$). Elemental analysis: C, 60.9; H, 4.6; and S, 5.9%. Formula $C_{28}H_{26}O_{10}S$ requires C, 60.6; H, 4.7; and S, 5.8%. ^{13}C-Nmr for **17** ($CDCl_3$): δ 77.7 (C-5), 74.7 (C-3), 71.0 (C-4), 70.0 (C-2), 68.7 (C-6), 68.2 (C-1), and 38.7 ppm (methanesulfonyl methyl carbon).

Anhydrous potassium thiocyanate (3.5 g) was added to a solution of **17** (4 g) in N,N-dimethylformamide (50 mL). The mixture was held at 90°C, with stirring, for 48 h. Progress of the reaction was monitored by tlc using chloroform-ethyl acetate (4:1, vol). The reaction mixture was poured slowly into stirred ice water, and the resulting crystals were recovered by filtration, washed with

water (50 mL), and dissolved in chloroform (50 mL). The chloroform solution was washed with water (3 x 200 mL) and concentrated *in vacuo* to a thick oil. Crystallization of the oil from methanol yielded 1,5-anhydro-2,3,4-tri-O-benzoyl-6-deoxy-6-thiocyanato-D-glucitol (**18**) (3.2 g, 86%); m.p. 63-65°C, $[\alpha]_D$ +30.1° (*c* 1.5, $CHCl_3$). Elemental analysis: C, 65.0; H, 4.6; N, 2.6; and S, 5.9%. Formula $C_{28}H_{23}O_7NS$ requires C, 65.0; H, 4.5; N, 2.7; and S, 6.2%. The IR spectrum showed an absorbance at 2157 cm^{-1}, indicative of the thiocyanato group.[37] The ^{13}C-nmr resonance ($CDCl_3$) for C-6 shifted to δ 37.0 ppm.

Compound **18** (3 g) was debenzoylated with sodium methoxide in methanol.[32] The product was purified by column chromatography on silica gel (Merck 60, 70-230 mesh) with ethyl acetate-ethanol (5:1, vol). Acetylation of the purified product with acetic anhydride in pyridine[35] followed by crystallization from absolute ethanol yielded the acetylated disulfide **19** (1.75 g, 87%), m.p. 160-160.5°C, $[\alpha]_D$ + 112° (*c* 1.5, $CHCl_3$). Elemental analysis: C, 47.1; H, 5.6; and S, 10.4%. Formula $C_{24}H_{34}O_{14}S_2$ requires C, 47.2; H, 5.6; and S, 10.5%. The chemical ionization - mass spectrum (ci-ms) had major peaks at m/e 611 (28%, M + 1) and 551 (70%, M-59). The IR spectrum was devoid of absorbances characteristic of thiols at 2500-2600 cm^{-1}.[37] The ^{13}C-nmr resonances ($CDCl_3$) of C-6 and C-6' were at δ 42.9 ppm.

The disulfide (**19**) (1.5 g) was dissolved in glacial acetic acid (60 mL) at 75°C and zinc dust (3 g) was added to the solution. The reduction was monitored by glc. After 3 h, the reaction solution was allowed to cool, poured into water (300 mL), and extracted with chloroform (4 x 25 mL). The combined chloroform extracts were washed with water (3 x 100 mL) and concentrated *in vacuo* to an oil. Crystallization of the oil from absolute ethanol yielded 2,3,4-tri-O-acetyl-1,5-anhydro-6-deoxy-6-thio-D-glucitol (**20**) (0.6 g, 80%); m.p. 94.5-96.5°C, $[\alpha]_D$ + 65.1° (*c* 1.5, $CHCl_3$). The ci-ms had major peaks at m/e 307 (21%, M + 1) and 247 (100%, M-59). The ^{13}C-nmr resonance ($CDCl_3$) of C-6 was at δ 27.3 ppm, as expected for thiol substitution.[37]

Deacetylation of **20** with methanolic sodium methoxide[32] and crystallization of the product from absolute ethanol yielded 1,5-anhydro-6-deoxy-6-thio-D-glucitol (**12**); m.p. 99.5-101°C, $[\alpha]_D$ + 53.7° (*c* 1.5, H_2O). Elemental analysis: C, 40.1; H, 6.8; and S, 17.3%. Formula $C_6H_{12}O_4S$ requires C, 40.0; H, 6.7; and S, 17.8%. The IR spectrum showed an absorbance at 2536 cm^{-1} characteristic of thiols.[37] ^{13}C-Nmr for **12** (D_2O): δ 81.3 (C-5), 78.5 (C-3), 72.9 (C-4), 70.6 (C-2), 70.1 (C-1), and 26.5 ppm (C-6). [Lit.[39] oil, $[\alpha]_D$ - 15° (*c* 1, MeOH)].

Acetylation of **12** with acetic anhydride-pyridine[9] gave 2,3,4-tri-O-acetyl-6-deoxy-6-S-acetyl-1,5-anhydro-D-glucitol (**21**); m.p. 87.5-88.5°C (from absolute EtOH), $[\alpha]_D$ + 29.9° (*c* 1.5 $CHCl_3$). Elemental analysis: C, 48.1; H, 5.8; and S, 9.1%. Formula $C_{14}H_{20}O_8S$ requires C, 48.3; H, 5.8; and S, 9.2%. The ci-ms had major peaks at m/e 349 (33%, M + 1) and 289 (100%, M-59). ^{13}C-Nmr for **21** ($CDCl_3$): δ 78.5 (C-5), 74.7 (C-3), 71.7 (C-4), 70.2 (C-2), 67.9 (C-1), and 31.3 ppm (C-6). [Lit.[39] oil, $[\alpha]_D$ + 60° (*c* 1, $CHCl_3$)].

Kinetic Analysis

All solutions were prepared under nitrogen using oxygen-free, triply-distilled water. Alkaline stock solutions were stored under nitrogen in paraffin-lined bottles. Stock sodium sulfide solution (2M) was prepared from washed, reagent grade sodium sulfide nonahydrate. Reaction solutions were prepared by diluting the stock solutions, and adding sodium p-toluenesulfonate as required. The volume expansivity of water[40] was used to calculate the concentrations required at room temperature to give the desired concentration at the selected reaction temperature. Sodium sulfide concentrations were determined from titrations with standard 0.1M mercuric chloride[41] followed with an Orion silver/sulfide specific electrode. The sodium hydroxide concentration in kraft liquors was calculated by subtracting the sulfide contribution from the active alkali.[42]

The reactor system, described in detail elsewhere,[11,27,43]

consisted of a Type 316 stainless steel reactor (100-mL capacity) from which samples (ca. 1 mL) could be withdrawn, and a constant temperature oil bath which would hold within 0.2°C of the desired temperature. The formation of ferric sulfide in the reactor was exceedingly slow compared to substrate degradation, and could be neglected.[27]

Sampling was initiated after the reactor had reached the desired temperature. 2-Hydroxyethyl 1-thio-β-D-glucopyranoside solution (0.005M, 1 mL) was added gravimetrically to the samples (1 mL) as an internal standard. The samples were then deionized by passage over Amberlite MB-3 (H^+, OH^-; 5 mL) or Amberlite IR-120 (H^+, 2.5 mL) resin, eluted with water (10 mL), concentrated in vacuo to dryness, and acetylated with acetic anhydride (0.33 mL) in pyridine (0.67). After 6 h, water (10 mL) was added to the acetylation, and the mixture was extracted with chloroform (2 x 5 mL). The chloroform extracts were washed with 1M hydrochloric acid (10 mL) and water (2 x 10 mL), and concentrated in vacuo to dryness. The residue was dissolved in chloroform (ca. 0.25 mL) for glc analysis. Response factors were obtained by subjecting known mixtures of the necessary compounds to the analysis procedure.

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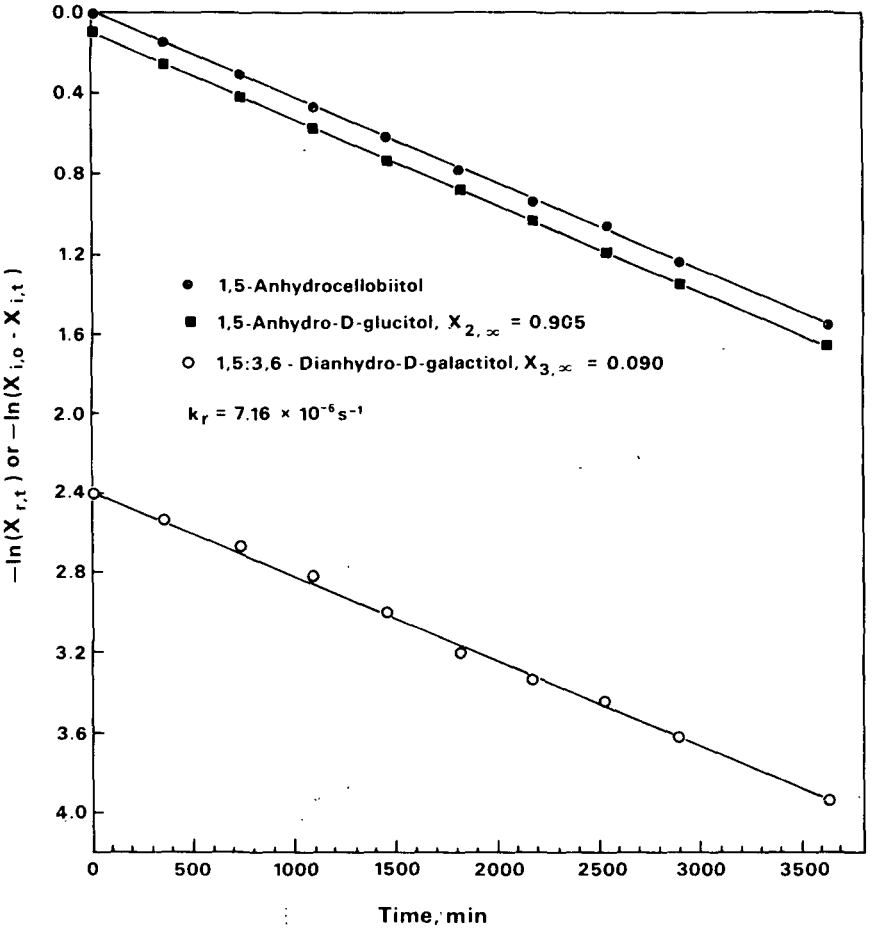

Figure 1. Parallel first-order kinetic analysis of the degradation of 1,5-anhydrocellobiitol (1) (0.01M) in 0.996M NaOH and 0.200M Na_2S at 170.5°C.

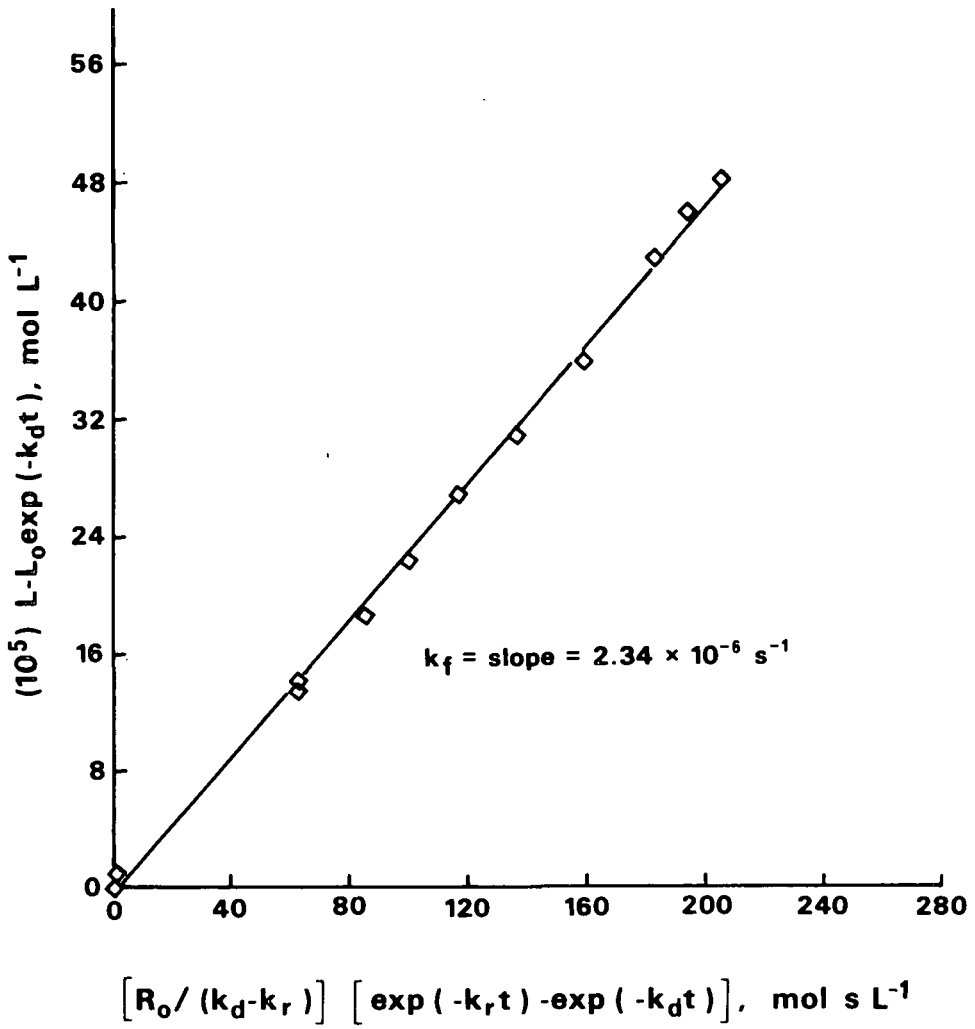

Figure 2. Determination of the rate constant (k_f) for formation of 1,6-anhydro-β-D-glucopyranose (4) from 1,5-anhydrocellobiitol (1) in 0.996M NaOH and 0.200M Na_2S at 170.5°C.

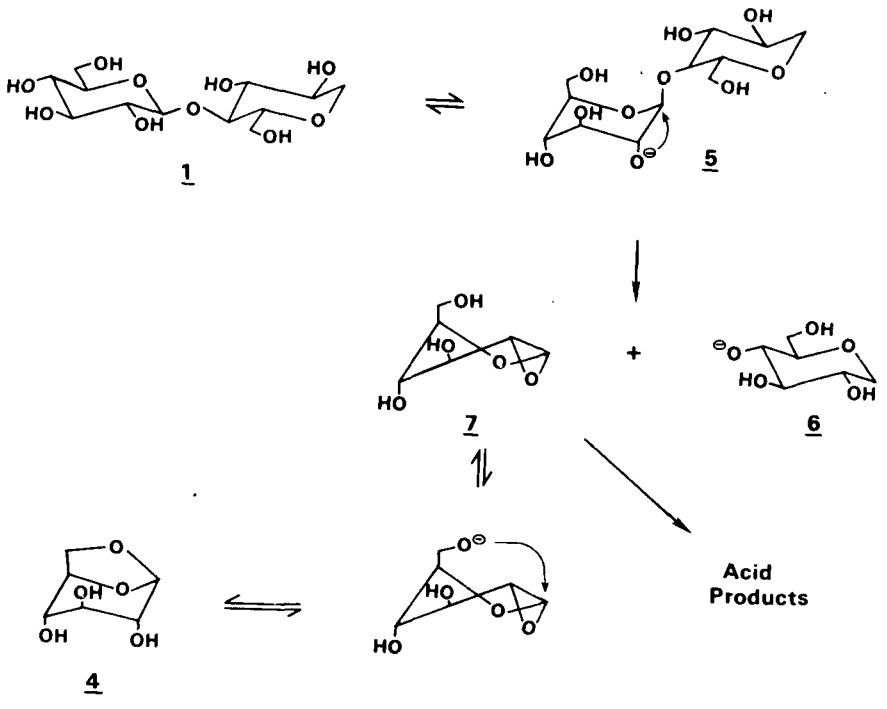

Figure 3. Potential $S_N$icB(2') mechanism for glycosyl-oxygen bond cleavage in 1,5-anhydrocellobiitol (1).[11]

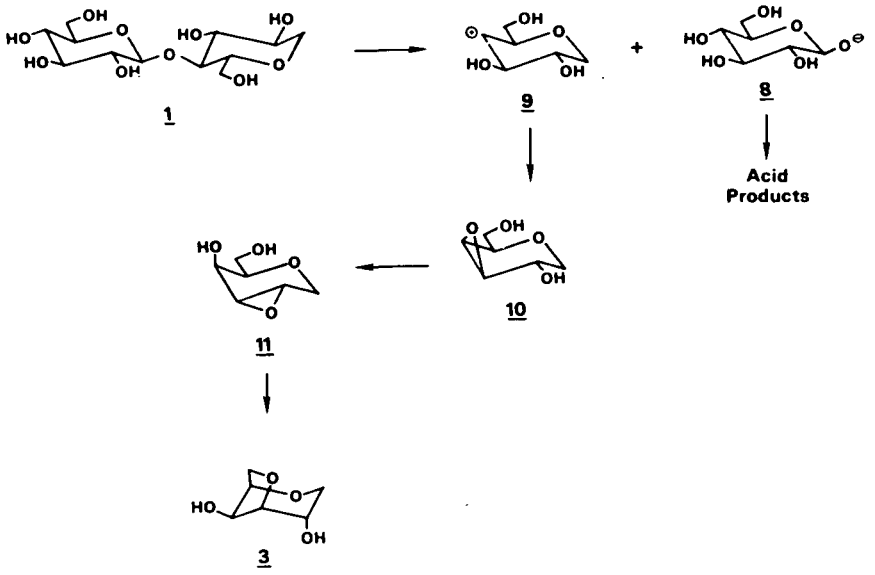

Figure 4. Potential S_N1 mechanism for oxygen-aglycon bond cleavage in 1,5-anhydrocellobiitol (1).[11]

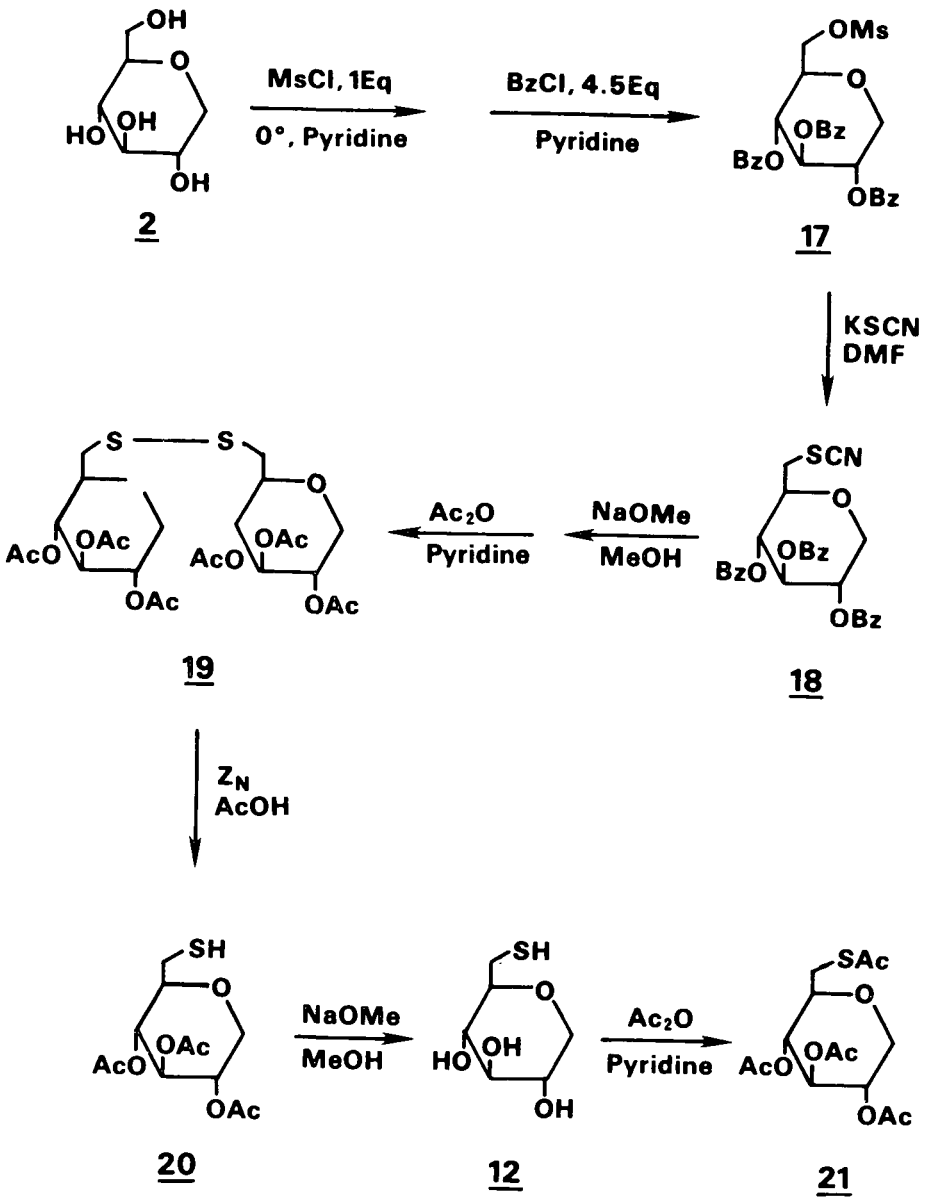

Figure 5. Synthesis of 1,5-anhydro-6-deoxy-6-thio-D-glucitol (12).